# PESTICIDE SURFACE WATER QUALITY REPORT

## MARCH 2001 SAMPLING EVENT


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**Pesticide Monitoring Project Report**
**March 2001 Sampling Event**

***Executive Summary***

As part of the District's quarterly ambient monitoring program, unfiltered water samples from 38 sites were collected from March 19 to March 21, 2001 and analyzed for over sixty pesticides and/or products of their degradation. The herbicides ametryn, atrazine, bromacil, diuron, norflurazon, prometryn, and simazine, along with the insecticides/degradates and fungicide atrazine desethyl, atrazine desisopropyl, diazinon, alpha endosulfan, beta endosulfan, endosulfan sulfate, ethoprop, imidacloprid, and metalaxyl were detected in one or more of these surface water samples.

Endosulfan (α and β), one of the pesticides for which a numerical criterion has been adopted under the Florida Class III Water Quality Standards for surface water (Chapter 62-302), was detected at three sites. The surface water concentration detected at G94D (0.153 μg/L) during this sampling event exceeds the Florida Class III surface water quality standard (Chapter 62-302) of 0.056 μg/L. This is the first water quality standard exceedance at this location. At this concentration, long term exposure can cause impacts to wildlife, but the pulsed nature of urban and agricultural runoff releases to the canal system precludes drawing any conclusions about long term average exposures.

The highest surface water concentrations of atrazine found in this sampling event (11 μg/L at S5A, 6.8 μg/L at S6, and 3.4 μg/L at S7) could inhibit algal cell multiplication. Possible impacts could occur to the base of the food chain.

The diazinon concentration of 0.15 μg/L at NSIDCW07 is greater than the chronic toxicity level (0.04 μg/L) for *Daphnia magna*, calculated according to the promulgated procedure (FAC 62-302.200). At this level, long-term exposure can cause adverse impacts to the macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about long term average exposures.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

***Background and Methods***

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimable) waters, while Lake Okeechobee is also protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-three pesticides and degradation products were analyzed for in samples from all of the 38 sites (Figure 1). Sites NSIDWC06 and NSIDWC07 were added to evaluate the surface water quality upstream of the S38B structure. The new sites divide the West Basin of the North Springs Improvement District into segments north (NSIDWC06) and south (NSIDWC07) of the Sawgrass Expressway. These two sites will be used to determine basin pesticide concentrations. The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FDEP, 1994) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest $EC_{50}$ or $LC_{50}$ reported in the summarized literature. These summary covers surface water samples collected between March 19 and March 21, 2001.

### *Findings and Recommendations*

At least one pesticide was detected in the surface water at 32 of the 38 sites. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program, with the exception of imidacloprid. Although imidacloprid has been analyzed in the surface water since the February 1997 sampling event, this is the first surface water detection.

Endosulfan (α plus β) was detected in the surface water at three sites during this sampling event. Although endosulfan was detected at S178, it did not exceed the Florida Class III surface water quality standard (Chapter 62-302) (Figure 3). The surface water concentration detected at G94D (0.153 µg/L) during this sampling event does exceed the Florida Class III surface water quality standard (Chapter 62-302) of 0.056 µg/L. This is the first water quality standard exceedance at this location.

The diazinon concentration detected (0.15 µg/L at NSIDWC07), should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, this level is greater than the calculated chronic toxicity (0.04 µg/L) for *Daphnia magna*, a sensitive indicator species for aquatic macroinvertebrates. This sampling site and NSIDWC06 were added to the network due to previous diazinon detections at the downstream sampling site (S38B). These locations have the potential for determining which upstream basin may be contributing diazinon to the surface water.

The highest surface water concentrations of atrazine found in this sampling event (11 µg/L at S5A, 6.8 µg/L at S6, and 3.4 µg/L at S7) could inhibit algal cell multiplication. Atrazine inhibits cell multiplication of the alga, *Microcystis aeruginosa*, at 3 µg/L. Possible impacts could occur to the base of the food chain.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

***Usage and Water Quality Impacts***

<u>Ametryn</u>: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour $LC_{50}$ of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.010 to 0.078 µg/L. Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

<u>Atrazine</u>: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour $LC_{50}$ of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow (Verschueren, 1983). Atrazine inhibits cell multiplication of the alga, *Microcystis aeruginosa*, at 3 µg/L and most other biological effects occur at higher concentrations (Verschueren, 1983). The atrazine surface water concentrations found in this sampling event at 29 of the 38 sampling locations, ranged from 0.012 to 11 µg/L. The highest surface water concentrations of atrazine found in this sampling event (3.4 µg/L at S7, 6.8 µg/L at S6, and 11 µg/L at S5A) could inhibit algal cell multiplication. Possible impacts could occur to the base of the food chain.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio, on a molar basis, (DAR) has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). No appreciable difference can be detected when the DAR is determined on the basis of flow or no flow (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

<u>Bromacil</u>: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour $LC_{50}$ of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.36 µg/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96-hour $LC_{50}$ of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48 hour $LC_{50}$ of 1.4 mg/L for water fleas and a 96 hour $LC_{50}$ of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). The highest concentration of diuron found during this sampling event was 0.39 µg/L (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae.

<u>Diazinon:</u> Diazinon is a non-systemic insecticide and acaricide registered for use on a wide range of crops including citrus, bananas, vegetables, potatoes, sugarcane, rice and ornamentals. Environmental fate and toxicity data in Tables 3 and 4 indicate that diazinon (1) is easily lost from soil by surface solution, with a moderate loss from leaching, and minimum loss from surface adsorption; (2) is slightly toxic to mammals and relatively toxic to fish; and (3) does not bioaccumulate significantly. The diazinon concentration detected (0.15 µg/L at NSIDWC07), should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, this level is greater than the calculated chronic toxicity (0.04 µg/L) for *Daphnia magna*, a sensitive indicator species for aquatic macroinvertebrates. This is the first time sampling at this location.

<u>Endosulfan</u>: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral $LD_{50}$ for rats of 70 mg/kg (Hartley and Kidd, 1987). The Soil Conservation Service rates endosulfan with an extra small potential

for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). β-endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. A bioconcentration factor of 1,267 indicates a low to moderate degree of accumulation in aquatic organisms (Lyman et al., 1990). Endosulfan (α plus β) was detected at three locations (Table 2). The surface water concentration detected at G94D (0.153 μg/L) during this sampling event exceeds the Florida Class III surface water quality standard (Chapter 62-302) of 0.056 μg/L. This is the first water quality standard exceedance at this location. Endosulfan was detected at S178, however, the concentration was less than the water quality criterion (Figure 3).

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). No FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate.

Ethoprop: Ethoprop is a non-systemic soil insecticide/nematicide used on many crops including potatoes, tomatoes, sugarcane and turf. Environmental fate and toxicity data in Tables 3 and 4 indicate that ethoprop (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is moderately toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. Aquatic invertebrate $LC_{50}$ toxicity ranges from 13 μg/L to 25.3 μg/L for ethoprop (U.S. Environmental Protection Agency, 1985). The only surface water concentration of ethoprop found in this sampling event was 0.13 μg/L at S5A. This concentration is below a level that would have an acute detrimental impact on fish or aquatic invertebrates.

Imidacloprid: Imidacloprid is a systemic insecticide registered for use on a variety of row crops and turfgrass applications as well as for flea control. Environmental fate and toxicity data in Tables 3 and 4 indicate that imidacloprid (1) is soluble in water; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. This is the first surface water detection of imidacloprid. The concentration of 1.0 μg/L detected at G94D is below a level that would have an acute detrimental impact on fish or aquatic invertebrates.

Metalaxyl: Metalaxyl is a systemic fungicide. Registered uses include potatoes, strawberries, citrus, avocados and vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metalaxyl (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metalaxyl detected was 0.054 μg/L at G94D (Table 2). Using these criteria, the concentrations of metalaxyl detected should not have an acute, harmful impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The $LC_{50}$ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.026 to 0.38 µg/L. Even at the highest concentration, this is three orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

Prometryn: Prometryn is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, beans, and peas (Hartley and Kidd, 1987). Environmental fate and toxicity data in Tables 3 and 4 indicate that prometryn: (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of prometryn detected was 0.027 µg/L at structure S6. Using these criteria, this level should not have an acute impact on fish.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour $LC_{50}$ of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate $LC_{50}$ toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The simazine surface water concentrations found in this sampling event ranged from 0.010 to 9.3 µg/L, below any level of concern for fish or aquatic invertebrates.

### *Quality Assurance Evaluation*

Five duplicate samples were collected at sites S176, S4, S65E, S8, and NSIDWC07. All the analytes detected in the surface water had precision ≤30% RPD with the exception of the atrazine detected at S176. No analytes were detected in the field blanks collected at G211, S5A, and S65E. All samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. All analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

### *Glossary*

$LD_{50}$: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

$LC_{50}$: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

$EC_{50}$: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:
The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:
The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.

PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.

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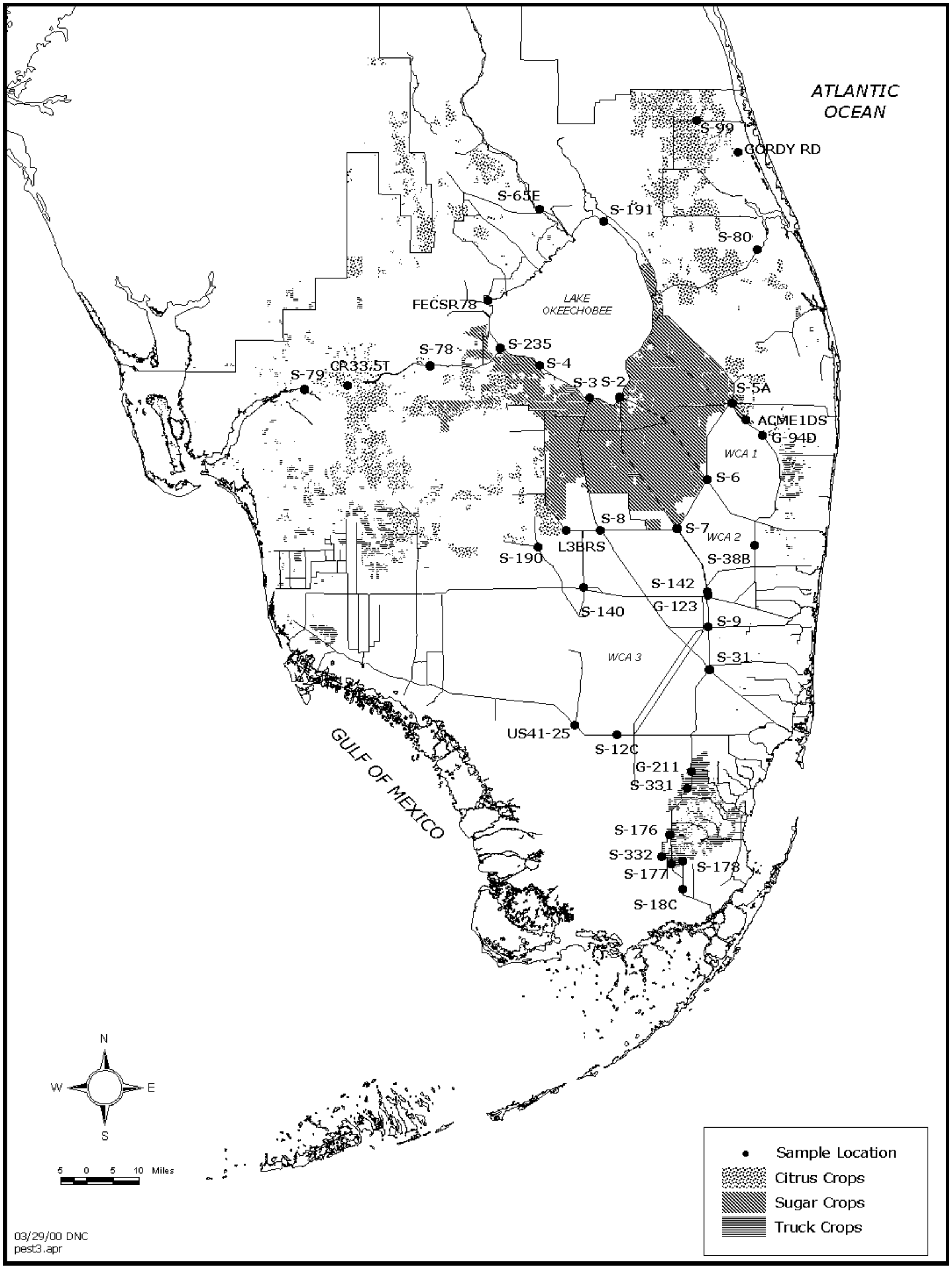


**Figure 1. SFWMD Pesticide Monitoring Network**

Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in March 2001.

| Pesticide or metabolite | Water range of MDL-PQL (µg/L) | Pesticide or metabolite | Water range of MDL-PQL (µg/L) |
|---|---|---|---|
| 2,4-D | 0.8 - 3.2 | α-endosulfan (alpha) | 0.0019 - 0.0104 |
| 2,4,5-T | 0.8 - 3.2 | β-endosulfan (beta) | 0.0019 - 0.0104 |
| 2,4,5-TP (silvex) | 0.8 - 3.2 | endosulfan sulfate | 0.0019 - 0.0264 |
| alachlor | 0.048 - 0.264 | endrin | 0.0019 - 0.0104 |
| aldrin | 0.00095 - 0.0052 | endrin aldehyde | 0.0019 - 0.0104 |
| ametryn | 0.0095 - 0.052 | ethion | 0.019 - 0.104 |
| atrazine | 0.0095 - 0.052 | ethoprop | 0.019 - 0.104 |
| atrazine desethyl | 0.0095 - 0.052 | fenamiphos (nemacur) | 0.029 - 0.156 |
| atrazine desisopropyl | 0.0095 - 0.052 | fonofos (dyfonate) | 0.019 - 0.104 |
| azinphos methyl (guthion) | 0.019 - 0. 104 | heptachlor | 0.00095 - 0.0052 |
| α-BHC (alpha) | 0.00095 - 0.0052 | heptachlor epoxide | 0.00095 - 0.0052 |
| β-BHC (beta) | 0.0019 - 0. 0104 | hexazinone | 0.019 - 0.104 |
| δ-BHC (delta) | 0.00095 - 0.0052 | imidacloprid | 0.2 - 0.4 |
| γ-BHC (gamma) (lindane) | 0.00095 - 0. 00384 | linuron | 0.2 - 0.4 |
| bromacil | 0.038 - 0. 212 | malathion | 0.029 - 0.156 |
| butylate | 0.019 - 0.104 | metalaxyl | 0.048 - 0.264 |
| carbophenothion (trithion) | 0.029 - 0. 156 | methoxychlor | 0.038 - 0.212 |
| chlordane | 0.0095 - 0. 052 | metolachlor | 0.057 - 0.44 |
| chlorothalonil | 0.019 - 0.104 | metribuzin | 0.019 - 0.104 |
| chlorpyrifos ethyl | 0.019 - 0.104 | mevinphos | 0.058 - 0.316 |
| chlorpyrifos methyl | 0.0095 - 0. 052 | mirex | 0.0019 - 0.0104 |
| cypermethrin | 0.048 - 0.264 | naled | 0.076 - 0. 44 |
| DDD-p,p’ | 0.0019 - 0.0104 | norflurazon | 0.019 - 0.104 |
| DDE-p,p’ | 0.0019 - 0.0104 | parathion ethyl | 0.019 - 0.104 |
| DDT-p,p’ | 0.0019 - 0.0104 | parathion methyl | 0.019 - 0.104 |
| demeton | 0.11 - 0.64 | PCB | 0.019 - 0.104 |
| diazinon | 0.019 - 0.104 | permethrin | 0.0048 - 0.0264 |
| dicofol (kelthane) | 0.019 - 0.104 | phorate | 0.029 - 0.156 |
| dieldrin | 0.0019 - 0.0104 | prometryn | 0.019 - 0.104 |
| disulfoton | 0.019 - 0.104 | simazine | 0.0095 - 3.8 |
| diuron | 0.2 - 0.4 | toxaphene | 0.071 - 0.396 |
| | | trifluralin | 0.0095 - 0.052 |

Table 2. Summary of pesticide residues above the method detection limit found in surface water samples collected by SFWMD in March 2001.

| DATE | SITE | FLOW | COMPOUNDS (µg/L) | | | | | | | | | | | | | | | | Number of compounds detected at site |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ametryn | atrazine | atrazine desethyl | atrazine desisopropyl | bromacil | diuron | diazinon | alpha endosulfan | beta endosulfan | endosulfan sulfate | ethoprop | imidacloprid | metalaxyl | norflurazon | prometryn | simazine | |
| 3/19/01 | S18C | N | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S178 | N | - | 0.015 I | - | - | - | - | - | 0.0088 | 0.0050 I | - | - | - | - | - | - | - | 3 |
| | S177 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S332 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S176* | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S331 | N | - | 0.012 I | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 |
| | G211 | Y | - | 0.017 I | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 |
| | US41-25 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S12C | N | - | 0.021 I | - | 0.011 I | - | - | - | - | - | - | - | - | - | - | - | - | 2 |
| | C25S99 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.38 | - | 0.029 I | 2 |
| | GORDYRD | N | - | - | - | 0.014 I | - | - | - | - | - | - | - | - | - | 0.16 | - | 0.13 | 3 |
| | S80 | N | - | 0.083 | 0.017 I | - | - | - | - | - | - | - | - | - | - | 0.17 | - | - | 3 |
| | S191 | N | - | 0.019 I | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 |
| | S2 | N | 0.010 I | 0.31 | 0.042 | 0.017 I | - | - | - | - | - | - | - | - | - | - | - | 0.012 I | 5 |
| | S3 | N | 0.011 I | 0.33 | 0.043 | 0.018 I | - | - | - | - | - | - | - | - | - | - | - | 0.013 I | 5 |
| | S4 | N | 0.013 *I | 0.28 * | 0.041 * | 0.016 *I | - | - | - | - | - | - | - | - | - | - | - | 0.014 *I | 5 |
| 3/20/01 | S31 | N | - | 0.013 I | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 |
| | S9 | Y | - | 0.092 | 0.0096 I | - | - | - | - | - | - | - | - | - | - | - | - | - | 2 |
| | G123 | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S142 | R | - | 0.015 I | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 1 |
| | S140 | N | - | - | - | - | - | - | - | - | - | 0.0077 I | - | - | - | - | - | - | 1 |
| | S190 | N | - | 0.044 | - | - | - | - | - | - | - | 0.014 I | - | - | - | 0.044 I | - | - | 3 |
| | L3BRS | N | - | 0.15 | 0.015 I | - | - | - | - | - | - | - | - | - | - | 0.038 I | - | - | 3 |
| | S8 | N | 0.018 *I | 0.32 * | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 2 |
| | S7 | Y | 0.066 | 3.4 | 0.073 | 0.015 I | - | - | - | - | - | - | - | - | - | - | - | 0.015 I | 5 |
| | S79 | N | - | 0.11 | 0.021 I | 0.017 I | 0.11 I | - | - | - | - | - | - | - | - | 0.17 | - | 0.10 | 6 |
| | CR33.5T | N | - | 0.11 | 0.019 I | 0.038 I | 0.36 | 0.39 I | - | - | - | - | - | - | - | 0.28 | - | 0.49 | 7 |
| | S78 | N | 0.016 I | 0.26 | 0.030 I | 0.015 I | 0.078 I | - | - | - | - | - | - | - | - | 0.026 I | - | 0.013 I | 7 |
| | S235 | N | 0.025 I | 0.053 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 2 |
| | FECSR78 | Y | - | 0.21 | 0.020 I | 0.020 I | 0.26 | - | - | - | - | - | - | - | - | 0.13 | - | 0.041 | 6 |
| | S65E | N | - | 0.012 *I | - | - | 0.073 *I | - | - | - | - | - | - | - | - | - | - | 0.019 *I | 3 |
| 3/21/01 | S38B | N | 0.013 I | 0.76 | 0.073 | 0.0098 I | - | 0.21 I | - | - | - | - | - | - | - | - | - | - | 5 |
| | NSIDWC06 | N | 0.017 I | 0.85 | 0.084 | 0.013 I | - | - | - | - | - | - | - | - | - | - | - | - | 4 |
| | NSIDWC07 | N | 0.019 *I | 2.7 * | 0.21 * | 0.025 *I | - | - | 0.15 * | - | - | - | - | - | - | - | - | 0.010 *I | 6 |
| | S6 | N | 0.078 | 6.8 | 0.14 | 0.029 I | - | - | - | - | - | - | - | - | - | - | 0.027 I | 0.023 I | 6 |
| | S5A | N | 0.041 | 11 | - | - | - | - | - | - | - | - | 0.13 | - | - | - | - | 9.3 | 4 |
| | ACME1DS | N | 0.031 I | 0.17 | 0.023 I | - | - | - | - | 0.013 | 0.011 | 0.014 I | - | - | - | - | - | - | 6 |
| | G94D | N | - | 0.088 | - | - | - | - | - | 0.076 | 0.077 | 0.11 | - | 1.0 | 0.054 I | - | - | - | 6 |
| Total number of compound detections | | | 13 | 29 | 16 | 14 | 5 | 2 | 1 | 3 | 3 | 4 | 1 | 1 | 1 | 9 | 1 | 14 | |

N – no Y – yes R – reverse ; - denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Selected properties of pesticides found in the March 2001 sampling event.

| Common name | FDEP Surface Water Standards 62-302 (µg/L) | Florida Ground Water Guidance Conc. (µg/L) | $LD_{50}$ acute rats oral (mg/Kg) (1) | EPA Carcinogenic Potential | Water Solubility (mg/L) (2, 3) | Koc (ml/g) (2, 3) | soil half-life (days) (2, 3) | SCS rating (2) LE | SA | SS | Bioconcentration Factor (BCF) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ametryn | | 63 | 1,110 | D | 185 | 300 | 60 | M | M | M | 33 |
| atrazine | - | 3** | 3,080 | C | 33 | 100 | 60 | L | M | L | 86 |
| bromacil | - | 90 | 5,200 | C | 700 | 32 | 60 | L | M | M | 15 |
| chlorpyrifos ethyl | - | 21 | 135 -163 | D | 2 | 6070 | 30 | S | M | M | 418 |
| diazinon | - | 6.3 | 240 - 480 | E | 40 | 570 | 40 | M | S | L | 77 |
| diuron | - | 14 | 3400 | D | 42 | 480 | 90 | M | M | L | 75 |
| endosulfan, alpha | 0.056 | 0.35 | 70 | - | 0.53 | 12400 | 50 | XS | L | M | 884 |
| endosulfan, beta | - | 0.35 | 70 | - | 0.28 | - | - | - | - | - | 1267 |
| endosulfan sulfate | - | 0.3 | - | - | 0.117 | - | - | - | - | - | 2073 |
| ethoprop | - | - | 62 | - | 750 | 70 | 25 | L | S | M | 15 |
| imidacloprid | - | - | 424 (6) | E | 510 (6) | - | - | - | - | - | 18 |
| metalaxyl | - | 420 | 669 | - | 7100 | 100 | 70 | L | M | M | 4 |
| norflurazon | - | 280 | 9,400 | C | 28 | 700 | 90 | M | M | L | 94 |
| prometryn | - | 28 | 5235 | - | 33 | 400 | 60 | M | M | L | 86 |
| simazine | - | 4** | >5,000 | C | 6.2 | 130 | 60 | L | M | M | 221 |

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large (L), medium (M), small (S) or extra small (XS)
Bioconcentration Factor (BCF) calculated as BCF = 10^(2.791 - 0.564 log WS) (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP surface water standards (12/96) for Class III water except Class I in ( )
**primary standard

(1) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.
(2) Goss, D. and R. Wauchope. (Eds.) (1992). The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure. Soil Conservation Service. Fort Worth, TX.
(3) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.
(4) Lyman,W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington, DC.
(5) U.S. Environmental Protection Agency (1996). Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B-96-002.
(6) U.S. Environmental Protection Agency (1994). Pesticide Fact Sheet: Imidacloprid

Table 4. Toxicity of pesticides found in the March 2001 sampling event to selected freshwater aquatic invertebrates and fishes (ug/L).

| Common name | 48 hr $EC_{50}$ Water flea *Daphnia Magna* | | acute toxicity (*) | chronic toxicity (*) | 96 hr $LC_{50}$ Fathead Minnow (#) *Pimephales Promelas* | | acute toxicity | chronic toxicity | 96 hr $LC_{50}$ Bluegill *Lepomis macrochirus* | | acute toxicity | chronic toxicity | 96 hr $LC_{50}$ Largemouth Bass *Micropterus salmoides* | acute toxicity | chronic toxicity | 96 hr $LC_{50}$ Rainbow Trout (#) *Oncorhynchus mykiss* | | acute toxicity | chronic toxicity | 96 hr $LC_{50}$ Channel Catfish *Ictalurus Punctatus* | | acute toxicity | chronic toxicity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ametryn | 28,000 | (6) | 9333 | 1400 | - | | - | - | 4100 | (4) | 1367 | 205 | - | - | - | 8800 | (4) | 2933 | 440 | - | | - | - |
| atrazine | 6900 | (6) | 2300 | 345 | 15,000 | (6) | 5000 | 750 | 16,000 | (4) | 5333 | 800 | - | - | - | 8800 | (4) | 2933 | 440 | 7600 | (4) | 2,533 | 380 |
| bromacil | - | | - | - | - | | - | - | 127,000 | (6) | 42,333 | 6350 | - | - | - | 36,000 | (6) | 12,000 | 1800 | - | | - | - |
| chlorpyrifos ethyl | 1.7 | (6) | 0.57 | 0.085 | 203 | (6) | 68 | 10 | 2.6 | (4) | 0.87 | 0.13 | - | - | - | 11 | (4) | 3.7 | 0.55 | 280 | (6) | 93 | 14 |
| | 0.1 | (6) | 0.03 | 0.005 | - | | - | - | 5.8 | (6) | 1.93 | 0.29 | - | - | - | - | | - | - | - | | - | - |
| diazinon | 0.8 | (1) | 0.3 | 0.04 | 7800 | (6) | 2600 | 390 | 168 | (1) | 55 | 8.4 | - | - | - | 90 | (1) | 23.3 | 3.5 | 1500 | (1) | 500 | 75 |
| | 0.9 | (8) | 0.3 | 0.045 | - | | - | - | 165 | (3) | 56 | 8.3 | - | - | - | 1650 | (3) | 550 | 83 | - | | - | - |
| | - | | - | - | - | | - | - | 16,000 | (4) | 5333 | 800 | - | - | - | 2900 | (4) | 967 | 145 | - | | - | - |
| diuron | 1400 | (6) | 467 | 70 | 14,200 | (6) | 4733 | 710 | 5900 | (4) | 1967 | 295 | - | - | - | 5600 | (4) | 1867 | 280 | - | | - | - |
| endosulfan | 166 | (6) | 55 | 8 | 1 | (1) | 0.3 | 0.05 | 1 | (1) | 0.33 | 0.05 | - | - | - | 1 | (1) | 0.33 | 0.050 | 1 | (1) | 0.3 | 0.05 |
| | - | | - | - | - | | - | - | 2 | (3) | 0.67 | 0.10 | - | - | - | 3 | (2) | 1 | 0.15 | 1.5 | (6) | 0.5 | 0.08 |
| | - | | - | - | - | | - | - | - | | - | - | - | - | - | 1 | (3) | 0.33 | 0.050 | - | | - | - |
| | - | | - | - | - | | - | - | - | | - | - | - | - | - | 0.3 | (5) | 0.10 | 0.015 | - | | - | - |
| ethoprop | 93 | (6) | 31 | 4.7 | - | | - | - | - | | - | - | - | - | - | 13,800 | (4) | 4600 | 690 | - | | - | - |
| imidacloprid | 85,200 | (10) | 28,400 | 4260 | - | | - | - | - | | - | - | - | - | - | 83,000 | (10) | 27,667 | 4150 | - | | - | - |
| metalaxyl | 28,000 | (6) | 9333 | 1400 | - | | - | - | 139,000 | (6) | 46,333 | 6950 | - | - | - | 132,000 | (6) | 44,000 | 6600 | - | | - | - |
| norflurazon | 15,000 | (6) | 5000 | 750 | - | | - | - | 16,300 | (6) | 5433 | 815 | - | - | - | 8100 | (6) | 2700 | 405 | >200,000 | (4) | >67,000 | >10,000 |
| prometryn | 18,590 | (6) | 6197 | 930 | - | | - | - | 10,000 | (4) | 3333 | 500 | - | - | - | 2500 | (4) | 833 | 125 | - | | - | - |
| simazine | 1,100 | (6) | 367 | 55 | 100,000 | (6) | 33,333 | 5000 | 90,000 | (4) | 30,000 | 4500 | - | - | - | 100,000 | (6) | 33,333 | 5,000 | - | | - | - |

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour $LC_{50}$ is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.


(1) Johnson, W. W. and M.T. Finley (1980). Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

(2) U.S. Environmental Protection Agency (1977). Silvacultural Chemicals and Protection of Water Quality. Seattle, WA. EPA-910/9-77-036.

(3) Schneider, B.A. (Ed.) (1979). Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003

(4) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.

(5) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.

(6) U.S. Environmental Protection Agency (1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, D.C.

(7) Verschueren, K. (1983). Handbook of Environmental Data on Organic Chemicals. Second Edition, Van Nostrand Reinhold Co. Inc., New York N.Y.

(8) U.S. Environmental Protection Agency (1972). Effects of Pesticides in Water: A Report to the States. U.S. Government Printing Office. Washington, D.C.

(9) Mayer, F.L., and M.R. Ellersieck. (1986). Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals. U.S. Fish and Wildlife Service, Publication No. 160

(10) U.S. Environmental Protection Agency (1994). Pesticide Fact Sheet: Imidacloprid

## Table 5. Atrazine Desethyl/Atrazine Ratio (DAR) Data.

| DATE | SITE | FLOW* | atrazine µg/L | Moles/L | atrazine desethyl µg/L | Moles/L | DAR |
|---|---|---|---|---|---|---|---|
| 03/19/01 | S80 | N | 0.083 | 3.85E-10 | 0.017 | 9.06E-11 | 0.2 |
| | S2 | N | 0.31 | 1.44E-9 | 0.042 | 2.24E-10 | 0.2 |
| | S3 | N | 0.33 | 1.53E-09 | 0.043 | 2.29E-10 | 0.1 |
| | S4 | N | 0.28 | 1.30E-09 | 0.041 | 2.19E-10 | 0.2 |
| | S9 | Y | 0.092 | 4.27E-10 | 0.0096 | 5.12E-11 | 0.1 |
| 03/20/01 | L3BRS | N | 0.15 | 6.95E-10 | 0.015 | 7.99E-11 | 0.1 |
| | S7 | Y | 3.4 | 1.58E-08 | 0.073 | 3.89E-10 | 0.0 |
| | S79 | N | 0.11 | 5.10E-10 | 0.021 | 1.12E-10 | 0.2 |
| | CR33.5T | N | 0.11 | 5.10E-10 | 0.019 | 1.01E-10 | 0.2 |
| | S78 | N | 0.26 | 1.21E-09 | 0.030 | 1.60E-10 | 0.1 |
| | FECSR78 | Y | 0.21 | 9.74E-10 | 0.020 | 1.07E-10 | 0.1 |
| 03/21/01 | S38B | N | 0.76 | 3.52E-09 | 0.073 | 3.89E-10 | 0.1 |
| | NSIDW006 | N | 0.85 | 3.94E-09 | 0.084 | 4.48E-10 | 0.1 |
| | NSIDW007** | N | 2.7 | 1.25E-08 | 0.21 | 1.12E-09 | 0.1 |
| | S6 | N | 6.8 | 3.15E-08 | 0.14 | 7.46E-10 | 0.0 |
| | ACME1DS | N | 0.17 | 7.88E-10 | 0.023 | 1.23E-10 | 0.2 |
| | | | | **DAR** | **all sites** | **flow only sites** | **no flow sites** |
| | | | | average | 0.1 | 0.1 | 0.1 |
| | | | | median | 0.1 | 0.1 | 0.1 |
| | | | | minimum | 0.0 | 0.0 | 0.0 |
| | | | | maximum | 0.2 | 0.1 | 0.2 |

**Average * N – no Y – yes R- reverse

Figure 2. Ethion Concentration in Surface Water at S99

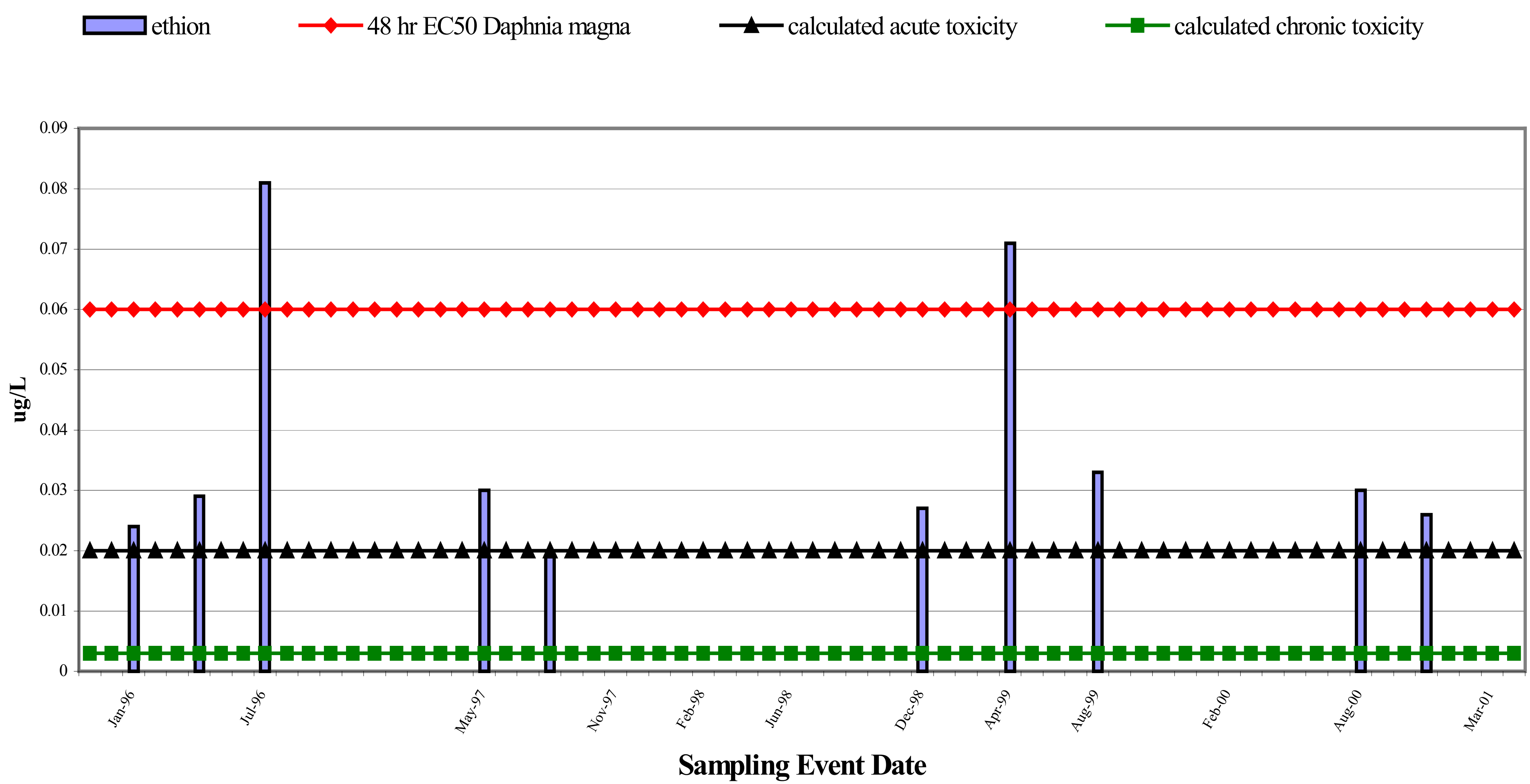

Figure 3. Endosulfan Concentration in Surface Water at S178